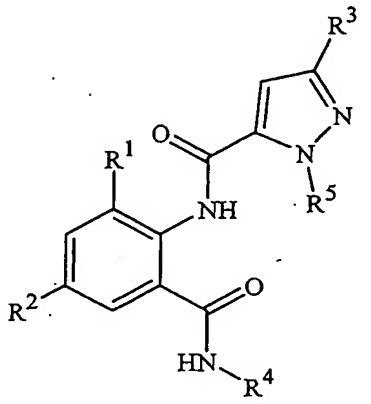
CLAIMS

What is claimed is:

1. A compound of Formula 1, an *N*-oxide or a salt thereof



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wherein

R^1 is Me, Cl, Br or I;

R^2 is -CN;

R^3 is Cl, Br, CF_3, OCH_2CF_3 or OCF_2H;

R^4 is H; or C_1–C_4 alkyl, C_2–C_4 alkenyl or C_2–C_4 alkynyl, each optionally substituted with CN or SMe; and

R^5 is phenyl substituted with 1 to 3 substituents selected from the group consisting of F, Cl, Br and Me.

2. The compound of Claim 1 wherein:

R^3 is Cl, Br or CF_3;

R^4 is Me, Et, *i*-Pr or *t*-Bu; and

R^5 is 2-chlorophenyl, 2-fluorophenyl, 2-bromophenyl, 2,4-dichlorophenyl, 2-chloro- 4-fluorophenyl, 2,6-dichlorophenyl, 2,6-difluorophenyl or 2,4,6-trichlorophenyl.

3. A composition for controlling an invertebrate pest comprising a biologically effective amount of a compound of Claim 1 and at least one additional component selected from the group consisting of a surfactant, a solid diluent and a liquid diluent, said composition optionally further comprising an effective amount of at least one additional biologically active compound or agent.

4. A composition of Claim 3 wherein at least one additional biologically active compound or agent is selected from insecticides of the group consisting of pyrethroids, carbamates, neonicotinoids, neuronal sodium channel blockers, insecticidal macrocyclic lactones, γ–aminobutyric acid antagonists, insecticidal ureas, juvenile hormone mimics, members of *Bacillus thuringiensis*, *Bacillus thuringiensis* delta endotoxin, and naturally occurring or genetically modified viral insecticides.

5. The composition of Claim 3 wherein the at least one additional biologically active compound or agent is selected from the group consisting of abamectin, acephate, acetamiprid, acetoprole, amidoflumet, avermectin, azadirachtin, azinphos-methyl, bifenthrin, bifenazate, bistrifluron, buprofezin, carbofuran, chlorfenapyr, chlorfluazuron, chlorpyrifos, chlorpyrifos-methyl, chromafenozide, clothianidin, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, cypermethrin, cyromazine, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, dinotefuran, diofenolan, emamectin, endosulfan, esfenvalerate, ethiprole, fenothicarb, fenoxycarb, fenpropathrin, fenvalerate, fipronil, flonicamid, flucythrinate, tau-fluvalinate, flufenerim, flufenoxuron, gamma-chalothrin, halofenozide, hexaflumuron, imidacloprid, indoxacarb, isofenphos, lufenuron, malathion, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, methoxyfenozide, metofluthrin, monocrotophos, methoxyfenozide, novaluron, noviflumuron, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, profluthrin, protrifenbute, pymetrozine, pyridalyl, pyriproxyfen, rotenone, spinosad, spiromesifen, sulprofos, tebufenozide, teflubenzuron, tefluthrin, terbufos, tetrachlorvinphos, thiacloprid, thiamethoxam, thiodicarb, thiosultap-sodium, tolfenpyrad, tralomethrin, trichlorfon, triflumuron, aldicarb, fenamiphos, amitraz, chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, etoxazole, fenazaquin, fenbutatin oxide, fenpyroximate, hexythiazox, propargite, pyridaben, tebufenpyrad, *Bacillus thuringiensis aizawai*, *Bacillus thuringiensis kurstaki*, *Bacillus thuringiensis* delta endotoxin, baculovirus, entomopathogenic bacteria, entomopathogenic virus and entomopathogenic fungi.

6. The composition of Claim 3 wherein the at least one additional biologically active compound or agent is selected from the group consisting of cypermethrin, cyhalothrin, cyfluthrin and beta-cyfluthrin, esfenvalerate,

fenvalerate, tralomethrin, fenothicarb, methomyl, oxamyl, thiodicarb, acetamiprid, clothianidin, imidacloprid, thiamethoxam, thiacloprid, indoxacarb, spinosad, abamectin, avermectin, emamectin, endosulfan, ethiprole, fipronil, flufenoxuron, triflumuron, diofenolan, pyriproxyfen, pymetrozine, amitraz, *Bacillus thuringiensis aizawai*, *Bacillus thuringiensis kurstaki*, *Bacillus thuringiensis* delta endotoxin and entomophagous fungi.

7. A method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a compound of Claim 1.

8. A method for controlling an invertebrate pest comprising contacting the invertebrate pest or its environment with a biologically effective amount of a composition of Claim 3.

9. The method of Claim 7 or Claim 8 wherein the invertebrate pest is a cockroach, an ant or a termite which is contacted by the compound by consuming a bait composition comprising the compound.

10. The method of Claim 7 or Claim 8 wherein the invertebrate pest is a mosquito, a black fly, a stable, fly, a deer fly, a horse fly, a wasp, a yellow jacket, a hornet, a tick, a spider, an ant, or a gnat which is contacted by a spray composition comprising the compound dispensed from a spray container.

11. The method of Claim 8 wherein a plant is contacted with the composition applied as a soil drench of a liquid formulation.

12. The composition of Claim 3 in the form of a soil drench liquid formulation.

13. A spray composition, comprising:
(a) a compound of Claim 1; and
(b) a propellant.

14. A bait composition, comprising:
(a) a compound of Claim 1;
(b) one or more food materials;

(c) optionally an attractant; and

(d) optionally a humectant.

15. A device for controlling an invertebrate pest, comprising:

(a) the bait composition of Claim 14; and

(b) a housing adapted to receive the bait composition, wherein the housing has at least one opening sized to permit the invertebrate pest to pass through the opening so the invertebrate pest can gain access to the bait composition from a location outside the housing, and wherein the housing is further adapted to be placed in or near a locus of potential or known activity for the invertebrate pest.

It is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. ^{1}H NMR spectra are reported in ppm downfield from tetramethylsilane; s is singlet, d is doublet, t is triplet, q is quartet, m is multiplet, dd is doublet of doublets, br s is broad singlet.

EXAMPLE 1

Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[4-cyano-2-methyl-6-[[(1-methylethyl)amino]-carbonyl]phenyl]-1*H*-pyrazole-5-carboxamide

Step A: Preparation of (2*E*)-[(2-chlorophenyl)hydrazono]acetic acid

To a solution of 2-chlorophenyl hydrazine hydrochloride (18.8 g, 0.105 mol) in water (300 mL) at room temperature was added concentrated hydrochloric acid (13.2 g, 0.136 mol), followed by dropwise addition over 20 minutes of 50% glyoxylic acid (17.1 g, 0.115 mol) to form a thick precipitate. The reaction mixture was then stirred for 30 minutes. The product was isolated by filtration, washed with water, and then dissolved in ethyl acetate (400 mL). The resulting solution was dried ($MgSO_4$) and concentrated under reduced pressure to afford the title product as a tan solid (20.5 g).

^{1}H NMR (Me_2SO-d_6) δ 12.45 (s, 1H), 10.7 (s, 1H), 7.59 (d, 1H), 7.54 (s, 1H), 7.40 (d, 1H), 7.23 (t, 1H), 6.98 (t, 1H).

Step B: Preparation of (2-chlorophenyl)carbonohydrazonic dibromide

To a solution of the product from Step A (20.5 g, 0.103 mol) in *N,N*-dimethylformamide (188 mL) at 0 °C was added *N*-bromosuccinimide (35.7 g, 0.206 mol) portionwise over 30 min. The resulting mixture was stirred overnight at ambient temperature. The reaction mixture was diluted with water (150 mL) and extracted with diethyl ether (3 x 200 mL). The combined organic extracts were dried ($MgSO_4$), absorbed onto silica gel and purified by chromatography to afford the title compound as a red oil (12.0 g).

^{1}H NMR ($CDCl_3$) δ 8.15 (br d, 1H), 7.41 (d, 1H), 7.31 (d, 1H), 7.21 (d, 1H), 6.90 (d, 1H).

Step C: Preparation of methyl 3-bromo-1-(2-chlorophenyl)-4,5-dihydro-1*H*-pyrazole-5-carboxylate

In a solution of the product from Step B (12.0 g, 38.5 mmol) in *N,N*-dimethylformamide (110 mL) was added methyl acrylate (13.85 mL, 153.8 mmol) in one portion, followed by dropwise addition of *N,N*-diisopropylethylamine (7.38 mL, 42.3 mmol) over 15 minutes. The reaction mixture was then stirred at ambient temperature for 1 h. The reaction mixture was diluted with water (200 mL) and extracted with diethyl ether (2 x 200 mL). The combined extracts were washed with water and brine. The ether extracts

for 20 hours. The reaction mixture was then cooled, and most of the dimethylformamide was removed by concentration on a rotary evaporator at reduced pressure. Water (200 mL) was added to the oily solid followed by ethylenediamine (20 mL), and the mixture was stirred vigorously to dissolve most of the solids. Residual solids were removed by filtration, and concentrated hydrochloric acid was added to the filtrate to adjust the pH to 5. As the pH decreased, some solids precipitated. The resulting mixture was partitioned between ethyl acetate and water. The separated organic solution was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residual solids were triturated with a mixture of ether, hexane and ethyl acetate to afford the title compound as a tan solid (7.61 g).
^{1}H NMR (Me_2SO-d_6) δ 7.97 (s, 1H), 7.50 (s, 1H), 7.3-7.5 (br s, 1H), 2.12 (s, 3H).

Step H: Preparation of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-8-methyl-4-oxo-4*H*-3,1-benzoxazine-6-carbonitrile

To a solution of 3-bromo-1-(2-chlorophenyl)-1*H*-pyrazole-5-carboxylic acid (i.e. the carboxylic acid product of Step E) (2.0 g, 6.29 mmol) and 2-amino-3-methyl-5-cyanobenzoic acid (i.e. the product of Step G) (1.1 g, 6.29 mmol) in acetonitrile (60 mL) at room temperature was added 3-picoline (3.2 mL, 32.7 mmol). The reaction mixture was stirred for 5 minutes and then cooled to –10 °C. Methanesulfonyl chloride (1.3 mL, 16.4 mmol) was then added dropwise, and after completion of the addition the reaction mixture was warmed to room temperature. On stirring overnight at room temperature, the reaction mixture formed a solid precipitate. The solid was isolated by filtration, washed with water, dissolved in excess methylene chloride and dried ($MgSO_4$). After removal of solvent, the residue was purified by chromatography on silica gel to afford the title compound (1.9 g).
^{1}H NMR ($CDCl_3$) δ 8.31 (s, 1H), 7.73 (s,1H), 7.45-7.6 (m, 4H), 7.31 (s,1H), 1.84 (s,1H).

Step I: Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[4-cyano-2-methyl-6-[[(1-methylethyl)amino]carbonyl]phenyl]-1*H*-pyrazole-5-carboxamide

To a solution of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-8-methyl-4-oxo-4*H*-3,1-benzoxazine-6-carbonitrile (i.e. the product of Step H) (2.7 g, 5.7 mmol) in acetonitrile (150 mL) was added dropwise isopropylamine (1.95 mL, 22.9 mmol) and then the reaction was warmed to about 50 °C using a water bath until all solids dissolved. The reaction mixture was stirred at ambient temperature for 2 hours. As the reaction progressed, a thick white solid formed. The solids were isolated by filtration and washed with diethyl ether and hexane to afford the title compound, a compound of the present invention, as a white solid (2.34 g) that melted at 145-149 °C.
^{1}H NMR ($CDCl_3$) δ 10.5 (br s, 1H), 7.59 (d, 1H), 7.56 (m, 2H), 7.4 (m, 3H), 7.02 (s, 1H), 5.98 (br d, 1H), 4.2 (m, 1H), 2.25 (s, 3H), 1.27 (d, 6H)

EXAMPLE 2

Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[4-cyano-2-methyl-6-[(methylamino)-carbonyl]phenyl]-1*H*-pyrazole-5-carboxamide

To a solution of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-8-methyl-4-oxo-4*H*-3,1-benzoxazine-6-carbonitrile (i.e. the product of Example 1, Step H) (2.7 g, 5.7 mmol) in acetonitrile (150 mL) was added dropwise methylamine (2.0 M solution in THF, 18.0 mL, 36.0 mmol), and the mixture was then stirred at room temperature for 30 minutes. As the reaction progressed, a thick white solid formed. The reaction mixture was cooled to 0 °C, and the solids were isolated by filtration and purified by silica gel chromatography to afford the title compound, a compound of the present invention, as a white solid (2.1 g) that melted at 242-243 °C.

^{1}H NMR ($CDCl_3$) δ 10.45 (br s, 1H), 7.5-7.6 (m, 3H), 7.4 (m, 3H), 7.03 (s, 1H), 6.3 (br d, 1H), 2.98 (d, 3H), 2.25 (s, 3H).

EXAMPLE 3

Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[2, 4-dichloro-6-[(methylamino)-carbonyl]phenyl]-1*H*-pyrazole-5-carboxamide

Step A: Preparation of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-6,8-dichloro-4*H*-3,1-benzoxazin-4-one

To a mixture of 3-bromo-1-(2-chlorophenyl)-1*H*-pyrazole-5-carboxylic acid (i.e. the carboxylic acid product of Example 1, Step E) (3.0 g, 9.44 mmol) and 3,5-dichloroanthranilic acid (1.94 g, 9.44 mmol) in acetonitrile (60 mL) was added 3-picoline (4.81 mL, 49.1 mmol) at room temperature, and the reaction mixture was stirred for 5 minutes. The reaction mixture was cooled to −10 °C and methanesulfonyl chloride (1.91 mL, 24.56 mmol) in acetonitrile (5 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The resulting solids were isolated by filtration, washed with water, then dissolved in excess methylene chloride and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residual solid was purified by chromatography on silica gel to afford the title compound (2.0 g).

^{1}H NMR ($CDCl_3$) δ 8.0 (s, 1H), 7.72 (s, 1H), 7.4-7.55 (m, 4H), 7.28 (s, 1H)

Step B: Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[2,4-dichloro-6-[(methylamino)carbonyl]phenyl]-1*H*-pyrazole-5-carboxamide

To a solution of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-6,8-dichloro-4*H*-3,1-benzoxazin-4-one (i.e. the product of Step A) (2.4 g, 8.8 mmol) in acetonitrile (150 mL) cooled to 0 °C was added dropwise methylamine (2.0 M solution in THF, 17.7 mL, 35.4 mmol), and the reaction mixture was stirred for 15 min. As the reaction progressed, a thick white solid formed. The solids were isolated by filtration and purified by silica gel

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EXAMPLE 1

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Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[4-cyano-2-methyl-6-[[(1-methylethyl)amino]-carbonyl]phenyl]-1*H*-pyrazol-5-carboxamide

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To a solution of 2-chlorophenyl hydrazine hydrochloride (18.8 g, 0.105 mol) in water (300 mL) at room temperature was added concentrated hydrochloric acid (13.2 g, 0.136 mol), followed by dropwise addition over 20 minutes of 50% glyoxylic acid (17.1 g, 0.115 mol) to form a thick precipitate. The reaction mixture was then stirred for 30 minutes. The product was isolated by filtration, washed with water, and then dissolved in ethyl acetate (400 mL). The resulting solution was dried ($MgSO_4$) and concentrated under reduced pressure to afford the title product as a tan solid (20.5 g).

^{1}H NMR (Me_2SO-d_6) δ 12.45 (s, 1H), 10.7 (s, 1H), 7.59 (d, 1H), 7.54 (s, 1H), 7.40 (d, 1H), 7.23 (t, 1H), 6.98 (t, 1H).

Step B: Preparation of (2-chlorophenyl)carbonohydrazonic dibromide

To a solution of the product from Step A (20.5 g, 0.103 mol) in *N,N*-dimethylformamide (188 mL) at 0 °C was added *N*-bromosuccinimide (35.7 g, 0.206 mol) portionwise over 30 min. The resulting mixture was stirred overnight at ambient temperature. The reaction mixture was diluted with water (150 mL) and extracted with diethyl ether (3 x 200 mL). The combined organic extracts were dried ($MgSO_4$), absorbed onto silica gel and purified by chromatography to afford the title compound as a red oil (12.0 g).

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In a solution of the product from Step B (12.0 g, 38.5 mmol) in *N,N*-dimethylformamide (110 mL) was added methyl acrylate (13.85 mL, 153.8 mmol) in one portion, followed by dropwise addition of *N,N*-diisopropylethylamine (7.38 mL, 42.3 mmol) over 15 minutes. The reaction mixture was then stirred at ambient temperature for 1 h. The reaction mixture was diluted with water (200 mL) and extracted with diethyl ether (2 x 200 mL). The combined extracts were washed with water and brine. The ether extracts

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Step I: Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[4-cyano-2-methyl-6-[[(1-methylethyl)amino]carbonyl]phenyl]-1*H*-pyrazol-5-carboxamide

To a solution of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-8-methyl-4-oxo-4*H*-3,1-benzoxazine-6-carbonitrile (i.e. the product of Step H) (2.7 g, 5.7 mmol) in acetonitrile (150 mL) was added dropwise isopropylamine (1.95 mL, 22.9 mmol) and then the reaction was warmed to about 50 °C using a water bath until all solids dissolved. The reaction mixture was stirred at ambient temperature for 2 hours. As the reaction progressed, a thick white solid formed. The solids were isolated by filtration and washed with diethyl ether and hexane to afford the title compound, a compound of the present invention, as a white solid (2.34 g) that melted at 145-149 °C.
^{1}H NMR ($CDCl_3$) δ 10.5 (br s, 1H), 7.59 (d, 1H), 7.56 (m, 2H), 7.4 (m, 3H), 7.02 (s, 1H), 5.98 (br d, 1H), 4.2 (m, 1H), 2.25 (s, 3H), 1.27 (d, 6H)

EXAMPLE 2

Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[4-cyano-2-methyl-6-[(methylamino)-carbonyl]phenyl]-1*H*-pyrazol-5-carboxamide

To a solution of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-8-methyl-4-oxo-4*H*-3,1-benzoxazine-6-carbonitrile (i.e. the product of Example 1, Step H) (2.7 g, 5.7 mmol) in acetonitrile (150 mL) was added dropwise methylamine (2.0 M solution in THF, 18.0 mL, 36.0 mmol), and the mixture was then stirred at room temperature for 30 minutes. As the reaction progressed, a thick white solid formed. The reaction mixture was cooled to 0 °C, and the solids were isolated by filtration and purified by silica gel chromatography to afford the title compound, a compound of the present invention, as a white solid (2.1 g) that melted at 242-243 °C.

^{1}H NMR ($CDCl_3$) δ 10.45 (br s, 1H), 7.5-7.6 (m, 3H), 7.4 (m, 3H), 7.03 (s, 1H), 6.3 (br d, 1H), 2.98 (d, 3H), 2.25 (s, 3H).

EXAMPLE 3

Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[2, 4-dichloro-6-[(methylamino)-carbonyl]phenyl]-1*H*-pyrazol-5-carboxamide

Step A: Preparation of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-6,8-dichloro-4*H*-3,1-benzoxazin-4-one

To a mixture of 3-bromo-1-(2-chlorophenyl)-1*H*-pyrazole-5-carboxylic acid (i.e. the carboxylic acid product of Example 1, Step E) (3.0 g, 9.44 mmol) and 3,5-dichloroanthranilic acid (1.94 g, 9.44 mmol) in acetonitrile (60 mL) was added 3-picoline (4.81 mL, 49.1 mmol) at room temperature, and the reaction mixture was stirred for 5 minutes. The reaction mixture was cooled to −10 °C and methanesulfonyl chloride (1.91 mL, 24.56 mmol) in acetonitrile (5 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. The resulting solids were isolated by filtration, washed with water, then dissolved in excess methylene chloride and dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residual solid was purified by chromatography on silica gel to afford the title compound (2.0 g).

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Step B: Preparation of 3-bromo-1-(2-chlorophenyl)-*N*-[2,4-dichloro-6-[(methylamino)carbonyl]phenyl]-1*H*-pyrazol-5-carboxamide

To a solution of 2-[3-bromo-1-(2-chlorophenyl)-1*H*-pyrazol-5-yl]-6,8-dichloro-4*H*-3,1-benzoxazin-4-one (i.e. the product of Step A) (2.4 g, 8.8 mmol) in acetonitrile (150 mL) cooled to 0 °C was added dropwise methylamine (2.0 M solution in THF, 17.7 mL, 35.4 mmol), and the reaction mixture was stirred for 15 min. As the reaction progressed, a thick white solid formed. The solids were isolated by filtration and purified by silica gel